CHUKA UNIVERSITY

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE

CHEM 221: PHYSICAL CHEMISTRY II

STREAMS: BSC (CHEM) **TIME: 2 HOURS**

DAY/DATE: MONDAY 08/4/2019 **11.30 A.M. – 1.30 P.M.**

INSTRUCTIONS: Answer question ONE and any other TWO questions

QUESTION ONE (30 MARKS)

(a) (i) Explain why the heat capacity at a constant volume (CV) value for N_2 is always found to be less than that of Cl_2 at ordinary temperature [3 marks]

(ii) A 2 m long tube is provided with inlets at both ends so that Hcl and NH_3 gases can be admitted simultaneously. Calculate the distance from Hcl inlet end to the tube at which NH_3O will first appear. If two gases are admitted at the same time, one from one end the other from the other end. [2 marks]

(iii) A flask contains 10^{20} molecules of He at 27°C. Determine the number of molecules having:

(I) Average kinetic energy [5 marks]
(II) 100 times average kinetic energy [1½ marks]

(b) If the temperature above which a Van der Waal gas cannot be liquefied is 32.3°C and minimum pressure to be applied at the temperature of liquefaction is 48.2 atm,

(i) Calculate the diameter of gas molecule [3½ marks]

(ii) Calculate "a" in Angstorm and hence pressure of 60gm of the gas at 27°C with a volume of 2 litres if its molecular weight is 30

$\{IA° = 10^{-10} m, b = effective\ volume\ per\ mole\ of\ th\ e\ gas, a = the\ constant\ of \propto o\ rtionality \wedge are\ t\ he$

[2½ marks]

(c) (i) predict whether the aqueous solutions of the following will be acidic, neural or alkaline: Ammonium acetate, Ammonium cyanide and Ammonium fluoride

[5 marks]

$\{K_{acetic\ acid} = K_{ammonia} = 1.75 x\ 10^{-5}, K_{HCN} = 6.2\ x 10^{-10}, K_{HF} = 6.8 x\ 10^{-4}\}$

(ii) Define the terms salt hydrolysis, hydrolytic constant and the degree of hydrolysis of a salt [1½ marks]

(iii) Derive an expression for the pH of an aqueous solution of CH_3COONH_4

[5½ marks]

(iv) Calculate the hydrolysis constant, the degree of hydrolysis and the pH of a 0.524M ammonium acetate solution [½ marks]

QUESTION TWO (20 MARKS)

(a) The solubility of Agcl is 10^{-5} mole/litre. Calculate the solubilities in

(i) Water [1 mark]

(ii) 0.01M Nacl [3 marks]

(iii) 0.01M $NaNO_3$ [1 mark]

(iv) 0.001 M Ca $(NO_3)_2$

Arrange the solubility of AgCl in decreasing order

$\{The\ Debye - H\acute{u}ckel\ constant\ A\ at\ 25° C = 0.51, \log Y_i = -Az + z - \sqrt{\mu}\,\mu = Ionic\ strentgh\}$

[2 marks]

(b) (i) State the applications of the dissociation theory (Arrhenius theory) of ionization [1 mark]

(ii) Explain to why PCl_5 is not an electrolyte despite the fact that PCl_5 reacts with water to form H_3PO_4 and HCl and the solution is electrically conducting [1½ marks]

(iii) Discuss how a solvent influences ionization of electrolytes [4½ marks]

(c) (i) With help of a suitable example, explain the importance of common ion effect in analytical chemistry laboratory [3½ marks]

(ii) A saturated solution of H_2S at 25°C is of the order of 0.1 molar. For H_2S, $K_1 = 9.1 \times 10^{-8}$ and $K_2 = 1.2 \times 10^{-15}$. Calculate the concentration of sulphide ions S^{2-} in this solution and indicate the effect of doubling H^+ ion concentration on the S^{2-} concentration. [2½ marks]

QUESTION THREE (20 MARKS)

(a) (i) Explain why it's necessary for the solid dissolved in the liquid solvent be non-volatile (in case of colligative properties) [1½ marks]

(ii) Prove that, for a solution of a solute in a non-polar solvent at a particular concentration, DT_b / Tb is independent of the nature of solvent

$\{R = 1.987\, cal\, K^{-1} mol^{-1}, DT_b = elevation\, of\, boiling\, point, T_b = boiling\, point\, of\, solution\}$

[1 mark]

(iii) Prove that, $Kf > Kb \{Kb = Ebullioscopic\ point, Kf = cryoscopic\, constant\}$

[2 marks]

(b) (i) Outline the main differences between Henry's law and Raout's law [3 marks]

(ii) Consider a lake that is in normal atmospheric condition. Determine the solubility of O_2 (g) at 25°C temperature and 1 atm atmospheric pressure considering the vapor pressure of water in the atmospheric as 0.0313 atm. Normal air is composed of 21% of O_2 (g)

$\{Henry's\, law\, constant\, of\, oxygen\, at\, 25\,^\circ C = 1.3\, x\, 10^{-3}\, mol\, L^{-1}\, atm^{-1}$

[1 mark]

(iii) Draw a labeled diagram showing the application of Raoult's law for a gaseous mixture composed of X and Y gases [2½ marks]

(iv) Calculate the vapour pressure of a solution made by dissolving 50.0g $CaCl_2$, $C_6H_{12}O_6$, in 500g of water. The vapour pressure of pure water is 47.1 torr at 37°C

[2 marks]

(c) (i) Explain the role of osmotic pressure in food preservation and give a suitable example [1½ marks]

(ii) Explain why a drip intravenous administration of fluids is made of a solution of NaCl at a particular concentration rather than pure water

[1 mark]

(iii) Calculate the osmotic pressure of a solution of 1.0g of glucose $(C_6H_{12}O_6)$ in 1500ml of water at 37°C [1½ marks]

(iv) Briefly explain various methods which are possible to ensure a patient receives enough oxygen during surgery and also state with reasons the method which is the most practical [1½ marks]

(v) The Henry's law constant for $N_2(g)$ at 298K is $6.8\,x\,10^{-4}\,mol\,L^{-1}\,atm^{-1}$. A diver descends to a depth where the pressure is 5 atm. If the divers body contains about 5L of blood, calculate the maximum amount of nitrogen gas dissolved in the divers blood at 1 atm and at 5 atm.

$Assume\ solubility\ of\ nitrogen \in water \wedge blood$
$(¿\ be\ the\ same)$ [1½ marks]

QUESTION FOUR (20 MARKS)

(a) (i) A solution containing 0.684 gm of cane sugar in 100gm of water freezes at -0.037° C while a solution containing 0.585 gm of NaCl in 100gm of water freezes at -0.342°C. Calculate Kf (cryoscopy constant), i (Van't Hoff Factor) and % dissociation of NaCl. $(Cane\ sugar \equiv C_{12}H_{22}O_{11})$

[2 marks]

(ii) An organic acid (molar mass = 60) associates in benzene to form a dimer when 1.66 gm of the acid is dissolved in 100g benzene, the boiling point of benzene is raised by 0.36°C. Calculate the Van't Hoff factor and the degree of association of the acid in benzene.

$(K_b(Ebullioscopic\ constant) = 2.6\,kg\,Kmol^{-1})$

[1½ marks]

(iii) A solution of KI is isotonic with a 0.01M solution of I_2 at 27°c. When equal volume of two solutions were mixed together, the Osmotic pressure

dropped by 18.5% of that of the individual solutions. Calculate the percentage of conversion of I^{-} to I_3^{-}. Assume that the solution behave ideally and the salts are completely dissociated.

[5½ marks]

(b) (i) State the principal difference between congruent and incongruent phase transformation

[1 mark]

(ii) List six merits and five demerits of phase rule [3½ marks]

(iii) Write short notes on the phase diagram of the magnesium zinc system [5 marks]

(c) An immiscible liquid A when steam distilled with water gave a distillate of 0.2 dm^3 which contained 0.0572 dm^3 of A. the observed boiling point for the distillation was 98.2°C and the atmospheric pressure was 758 mm Hg. The vapour pressure of water at 98.2°C was 712 mm Hg. The relative density of the liquid was found to be 1.83. Calculate the molar mass of the unknown liquid. [1½ marks]
